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(54) **Determining oxygen metal ratio in nuclear fuel oxides**

(57) A method for determination of oxygen-to-metal ratio in a nuclear fuel oxide. The method comprises placing a mixture of a nuclear fuel oxide and a metal flux in a graphite crucible, heating said mixture in said crucible in a reducing atmosphere of an inert gas to melt said mixture thereby generating carbon monoxide, accurately determining an amount of the generated carbon monoxide to calculate an amount of oxygen in said oxide, and calculating oxygen-to-metal ratio in said oxide based on the calculated amount of oxygen.

keine Indikation: O_2/allotallgemein
kein O^{18} O^{16} Trennung
andere Thermokin
keine Analyse über Gemenge

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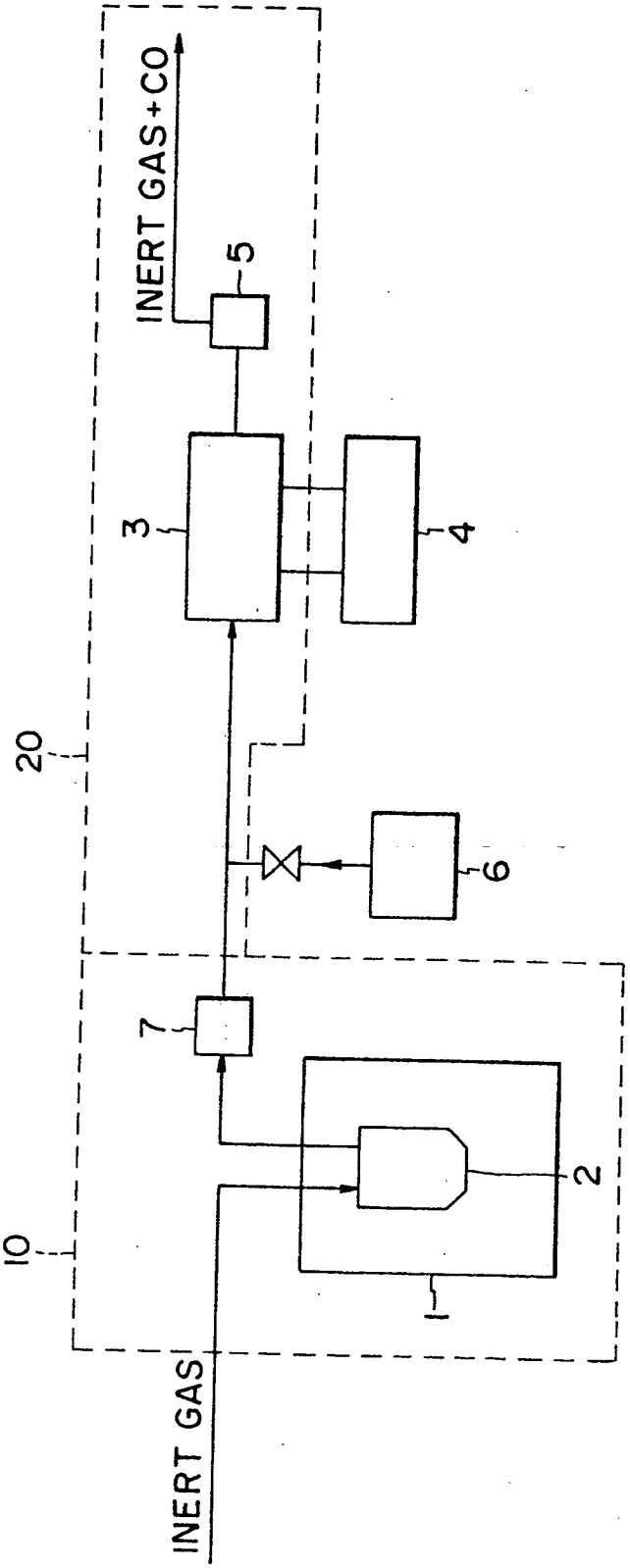
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SPECIFICATION

Method for determining oxygen-to metal ratio in nuclear fuel oxide

Background of the invention

The present invention relates to a method for rapid determination of oxygen-to-metal ratio (hereinafter referred to as "O/M ratio") in a nuclear fuel oxide with excellent accuracy.

It is no exaggeration to say that the O/M ratio in a nuclear fuel oxide such as uranium oxide, plutonium oxide, thorium oxide, or the like is an important physical property which influences the thermal conductivity, creep rate, diffusion of nuclear fission products, electrical conductivity, self-diffusion, etc. and determines the value of the nuclear fuel oxide.

For example, when M is U (uranium), the creep rate varies depending on the O/U ratio. Namely, the larger the O/U ratio, the larger the creep rate. Further, it is known that the larger the O/U ratio, the larger the electrical conductivity and the smaller the activation energy. It is also known that the larger the O/U ratio, the smaller the value of $\int_{Ts}^{Tc} k(T)dT$ which indicates the value necessary for causing melting or recrystallization. $\int_{Ts}^{Tc} k(T)dT$ is a so-called thermal conductivity integral wherein k(T) is the thermal conductivity at a temperature of T, Ts the temperature of a fuel element on its surface and Tc the temperature of a fuel element at its central part.

Examples of the methods for determining the O/M ratio in a nuclear fuel which have conventionally been adopted include an X-ray diffractometry in which the amount of oxygen present in the oxide is determined from the lattice constant and a gravimetry in which the increase and decrease in the amount of oxygen due to a redox reaction is determined with a balance.

However, in the above-mentioned conventional methods, the amount of oxygen is indirectly determined from the physical properties of a nuclear fuel oxide. Therefore, the conventional methods are disadvantageous in that errors of determination are large and that much time is needed for analysis and determination.

Summary of the invention

Accordingly, an object of the present invention is to provide a method capable of directly determining the O/M ratio in a nuclear fuel oxide with high accuracy and efficiency in a shortened period of time.

In accordance with the present invention, a nuclear fuel oxide is placed in a graphite crucible together with a metal flux and the mixture of the oxide and the metal flux in the crucible is heated in a reducing atmosphere of an inert gas such as argon or helium to thereby melt the mixture. Oxygen generated from the oxide by the reductive reaction immediately reacts with carbon of the graphite crucible to form carbon monoxide. Thus, the amount of oxygen can be calculated by accurately determining the amount of the generated carbon monoxide, and the O/M ratio can be calculated from the amount of oxygen.

A powder of a metal such as iron or tin may be used as the metal flux to be mixed with the nuclear fuel oxide. The use of such metal flux serves to lower the melting temperature of the nuclear fuel oxide and improve the uniformity of the melting.

Preferred apparatus for determining the amount of carbon monoxide include a non-dispersive infrared gas analyzer which takes advantage of infrared absorption by carbon monoxide and a thermal conductivity detector which takes advantage of the difference in the thermal conductivity between a carrier gas comprising an inert gas and carbon monoxide.

Brief description of the drawing

By way of example and to make the description more clear, reference is made to the accompanyng drawing which is an illustration of an apparatus for practicing the method of the present invention.

Preferred embodiments of the invention

Referring now to the accompanying drawings, the reference numeral 1 designates a gas extraction furnace within which a graphite crucible 2 is placed. The gas extraction furnace is constructed so that the contents of the graphite crucible 2 are melted with a heating apparatus (not shown). Examples of the heating apparatus include a high-frequency heating apparatus and a resistance heating constant-voltage power source using the graphite crucible as a resistor.

A mixture of a nuclear fuel oxide, e.g. uranium dioxide, with a metal flux, e.g. an iron powder, is placed in the graphite crucible 2. Then, an inert gas, e.g. argon is introduced into the gas extraction furnace, and the mixture in the crucible 2 is heat-melted in an argon atmosphere. In this connection, it is noted that, as mentioned above, the melting temperature of the nuclear fuel oxide can be lowered by adding a metal flux. For example, when uranium dioxide is used alone, it begins to melt at a temperature as high as 2850°C. On the other hand, by adding a metal flux, it begins to melt at about 2500°C.

Oxygen is generated from the oxide by a reductive reaction accompanying the melting of the oxide and metal flux. Due to the presence of the reducing atmosphere comprising argon, the generated oxygen immediately reacts with carbon of the graphite crucible 2 to form carbon monoxide. The reaction can be expressed by the following reaction formula:

$$MO_2 + \text{flux} + 2C\ (\text{carbon of graphite crucible}) \xrightarrow{\text{reductive reaction}} M\cdot\text{flux} + 2CO$$

wherein MO_2 stands for a nuclear fuel oxide, flux a powdered metal flux such as iron or tin, C carbon and CO carbon monoxide.

The carbon monoxide thus formed is passed together with argon from the gas extraction furnace 1 through a dust filter 7 and then introduced into a carbon monoxide determining apparatus 3 such as a non-dispersive infrared gas analyzer, where the amount of carbon monoxide contained in argon is accurately determined. If necessary, the determined value is recorded with a recorder 4. A mixed gas comprising carbon monoxide and argon discharged from the carbon monoxide determining apparatus 3 is released through a gas flowmeter 5 to the outside.

The gas flowmeter 5 is installed as an aid in monitoring whether the flow rate of the carrier gas (inert gas) is kept constant. With regard to the above-mentioned discharge of the mixed gas to the outside, it is noted that in the case of the analysis of a sample before irradiation (i.e., a sample of UO_2 before irradiation), it will suffice if a dust filter 7 is installed since oxygen is not in an activated state. However, in the case of the analysis of an irradiated sample, there are possibilities that the sample contains an FP gas (nuclear fission product gas) and that oxygen contained therein is in an activated state. Therefore, in such a case, an infallible filter means, e.g. a HEPA filter or an activated carbon filter, should be employed.

In the determination of the O/M ratio in a sample of a mixed oxide of PuO_2-UO_2, the gas extraction furnace 1 and carbon monoxide determining apparatus 3 should be provided within a glove box 10 and an open port box 20 which are indicated with a dotted line in the drawing.

The reference numeral 6 designates a standard gas generator which is used in calibrating the carbon monoxide determining apparatus 3. Namely, a mixed gas comprising a carbon monoxide gas and an inert gas, the carbon monoxide concentration of which is known, is preliminary run as a standard gas from the generator 6 to the carbon monoxide determining apparatus 3 to obtain response data indicated by the determining apparatus 3. The obtained data are graphed, and the linearity of the graph is examined to use the results in calibration.

The amount of oxygen C_O (% by weight) can be calculated based on the amount of carbon monoxide C_{CO} (% by weight) determined with the carbon monoxide determining apparatus 3 by the following equation (1):

$$C_O = \frac{W_O}{W_C + W_O} \times C_{CO} \qquad \ldots (1)$$

wherein W_O stands for the atomic weight of oxygen and W_C the atomic weight of carbon.

The O/M ratio R can be determined from the amount of oxygen C_O obtained by the equation (1), by the following equation (2):

$$C_O = \frac{W_O \cdot R}{W_M + W_O \cdot R} \times 100$$

$$\therefore R = \frac{C_O \cdot W_M}{100 - C_O} \cdot \frac{1}{W_O} \qquad \ldots (2)$$

wherein W_M stands for the average atomic weight of the metal atom M in an oxide MO_2.

It is also possible to automatically calculate the O/M ratio by programming the above-mentioned equations (1) and (2) into a data processor (not shown) and inputting the data, which have been determined with the carbon monoxide determining apparatus 3, into the data processor.

Further, it is possible to continuously and automatically carry out the determination according to the present invention by preliminarily placing various mixtures of a nuclear fuel oxide to be determined and a metal flux in a plurality of graphite crucibles respectively, disposing the crucibles on a turn table and supplying the crucibles one by one in each test succesively to the gas extraction furnace by the rotation of the the turn table.

As explained above, according to the present invention, the O/M ratio can be directly determined by extracting the whole quantity of oxygen in a nuclear fuel oxide, which leads to an improvement in accuracy of determination over the conventional O/M ratio determination methods. Further, since the process comprising the melting of a sample of a nuclear fuel oxide, fermentation of carbon monoxide and determination can be completed in a rate of about 10 minutes per sample, the present invention can remarkably shorten the determining time of the conventional methods which require about 7 hours to 1 day per sample. Further, the amount of the nuclear fuel oxide to be used as a sample may be about 0.1 to 0.5 g, i.e., can be reduced to 1/10 to 1/2 of those required in the conventional methods. The present invention also has an advantage that the dose of exposure resulting from the handling of a nuclear fuel oxide can be reduced by virtue of the shortened determining time and decrease in the amount of sample to be used.

Although the method of the present invention is particularly effective in determining the amount of oxygen and the O/M ratio in a nuclear fuel oxid , it is also applicable to the determination of the amount of oxygen and the O/M ratio in various oxides.

The foregoing description illustrates specific embodiments within the scope of this invention and are not to be construed as limitating said scope. It is to be understood that variations and modification thereof may be made by those skilled in the art without departing from the scope of the invention.

CLAIMS

1. A method for determination of oxygen-to-metal ratio in a nuclear fuel oxide, said method comprising placing a mixture of a nuclear fuel oxide and a metal flux in a graphite crucible,

heating said mixture in said crucible in a reducing atmosphere of an inert gas to melt said mixture thereby generating carbon monoxide,

accurately determining an amount of the generated carbon monoxide to calculate an amount of oxygen in said oxide, and

calculating oxygen-to-metal ratio in said oxide based on the calculated amount of oxygen.

2. The method according to claim 1, wherein said nuclear fuel oxide is selected from a group consisting of uranium oxide, plutonium oxide, thorium oxide and a uranium-plutonium mixed oxide.

3. The method according to claim 1, wherein said metal flux is selected from a group consisting of iron powder and tin powder.

4. The method according to claim 1, wherein said inert gas is selected from a group consisting of argon and helium.

5. The method according to claim 1, wherein said mixture of the nuclear fuel oxide and the metal flux is heated by high-frequency heating or resistance heating.

6. The method according to claim 1, wherein the amount of carbon monoxide is determined by using a non-dispersive infrared gas analyzer or a thermal conductivity detector.

7. A method according to claim 1, substantially as hereinbefore described with reference to and as shown in the accompanying drawing.

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